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(54) Metal diffusion process

(57) A process for the production of a diffusion coating which comprises contacting a part which is to be diffusion coated with a coating-producing composition while heating by high frequency induction heating, the coating being produced by the heating and the coating-producing composition being a loose powder composition which is retained in contact with the part which is to be diffusion coated by mechanical means during the heating is disclosed.

The induction heating may be provided by the use of an induction coil with a separator; the part to be diffusion coated, in particular chromised, may move through the said coil or the said coil may be inserted in the said part to be coated. Localised or overall coating may be provided.

The present invention has a number of advantages over the prior art, *inter alia,* in terms of cost and convenience.

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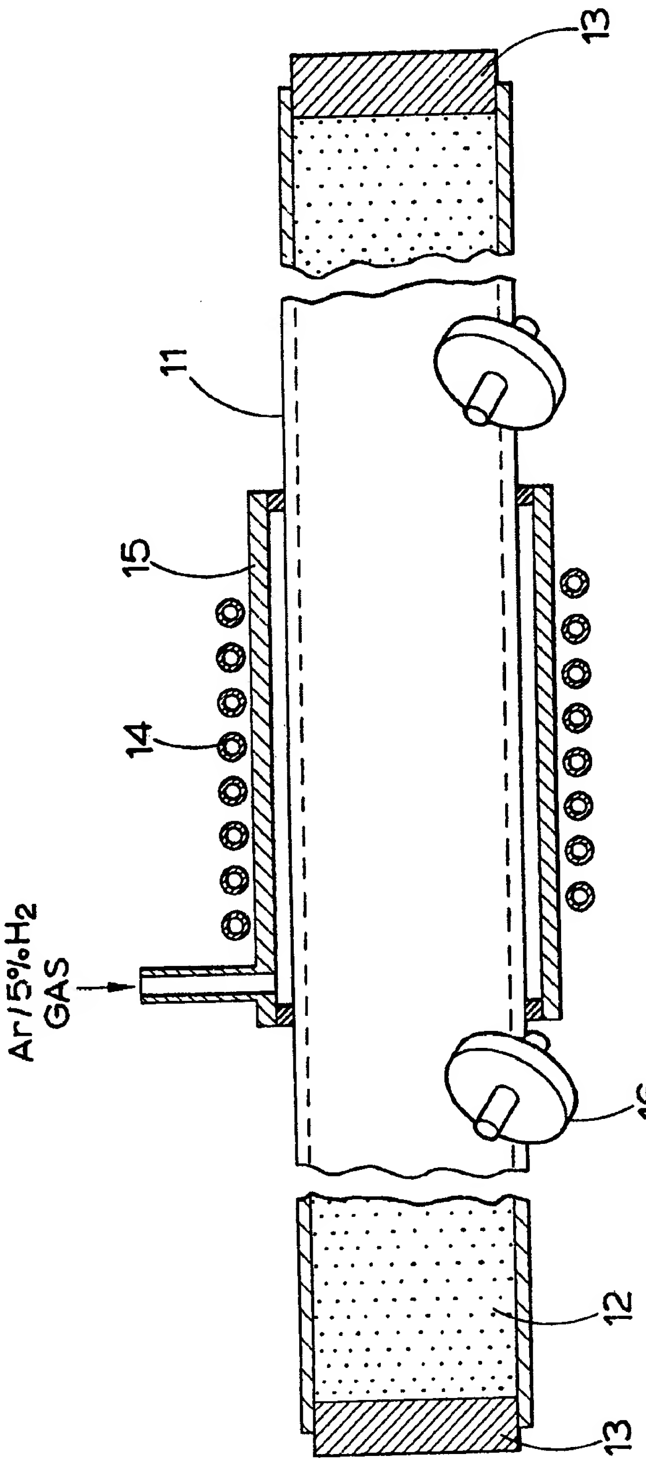
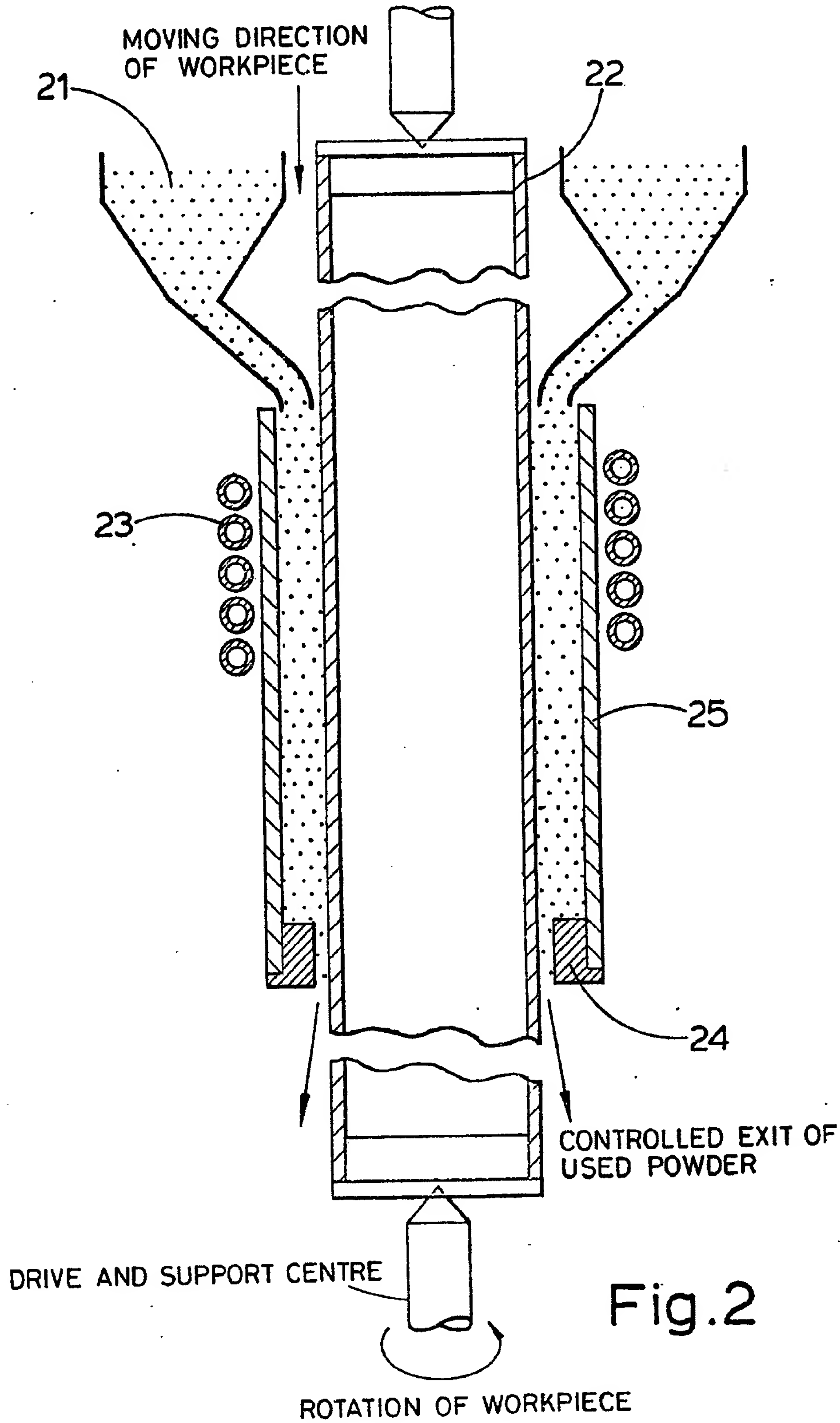


Fig.1


MOVING DIRECTION
OF WORKPIECE
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CONTROLLED EXIT OF
USED POWDER
DRIVE AND SUPPORT CENTRE
ROTATION OF WORKPIECE

Fig.2

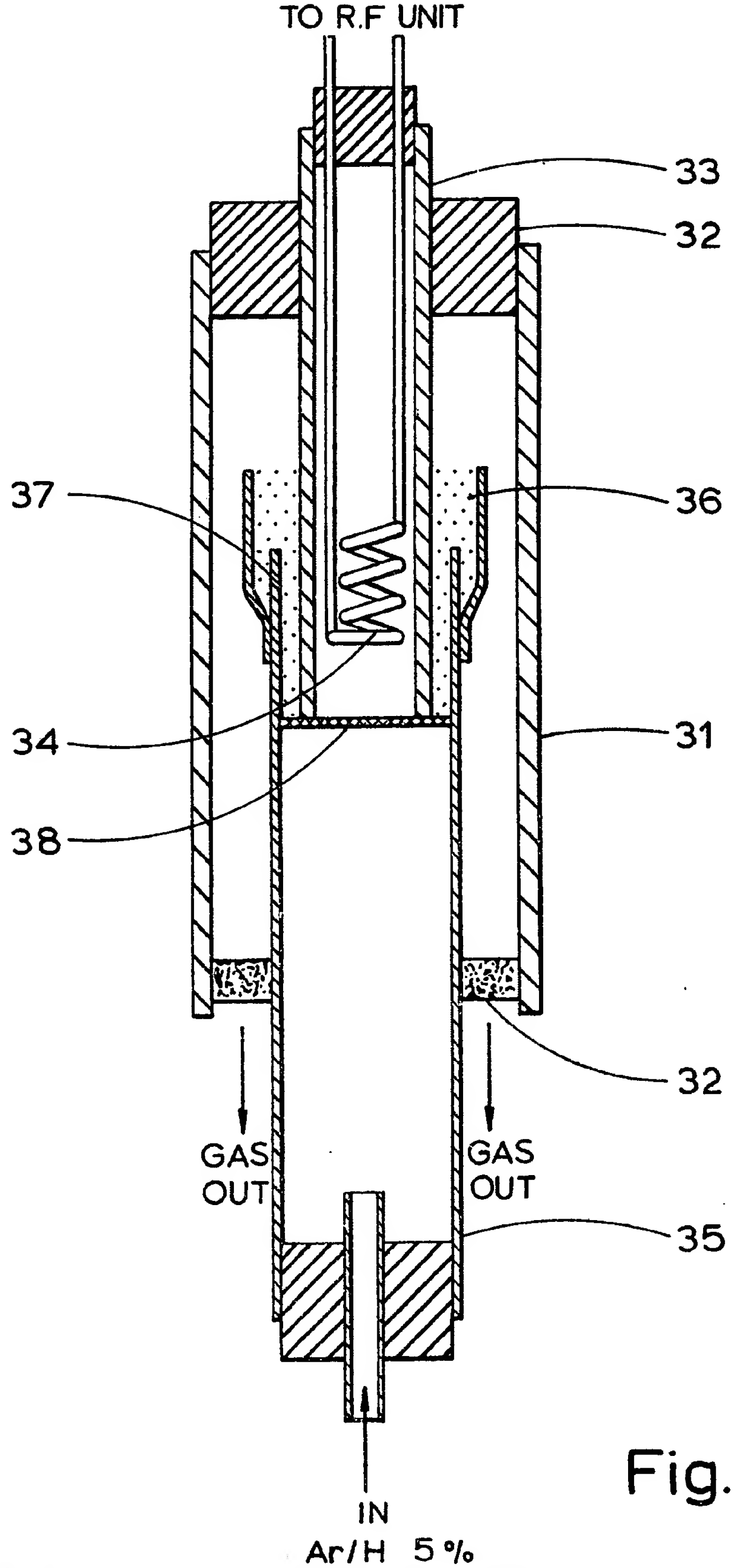

Fig.3

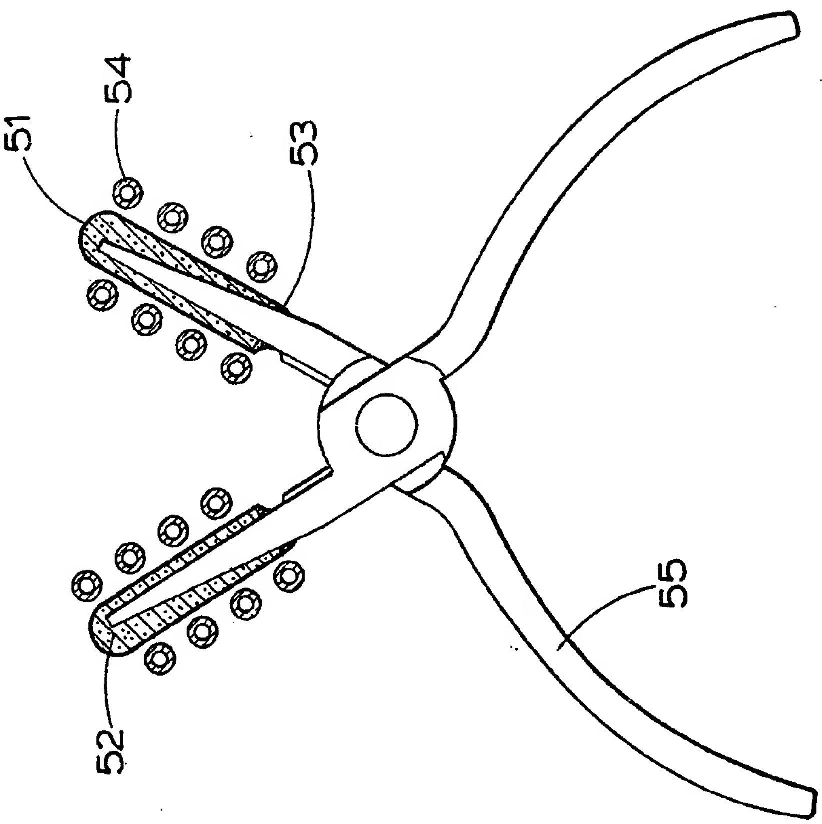

Fig.5

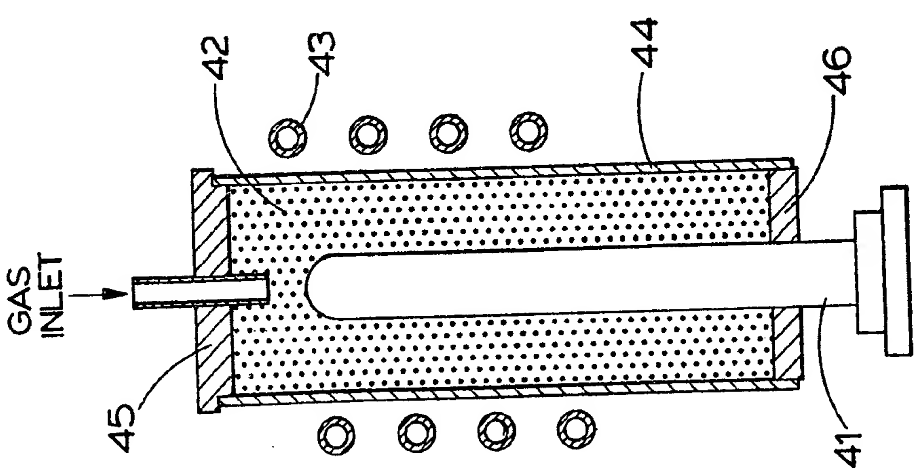

Fig.4

SPECIFICATION
Metal diffusion process

This invention relates to a metal diffusion process; more particularly, it relates to a process for producing diffusion coatings.

In the basic process of diffusing one metal into another, there is provided a powder containing the diffusing metal, commonly chromium or aluminium, either alone or in combination, together with a refractory diluent, such as alumina, and an energizer, usually a halide combined in some suitable form, such as an ammonia derivative. Other examples of metals and non-metals capable of diffusion for coating purposes are silicon, boron, manganese, titanium, vanadium, zirconium, hafnium and niobium. The powder is placed in a sealed box together with the metal part being coated and the box is introduced into a furnace for a period of time depending upon the size of the box, but which could be many hours. Under the influence of high temperatures, metallic halides are generated. These subsequently decomposed on the surface of the metal part being coated, depositing metal atoms. The resulting diffusion gradient is the driving force for the absorption of metal atoms into the part being coated. The process is expensive in terms of energy (heat) because powder is heated which is not strictly required for the process and also the box itself which contains the powder and parts, but which strictly takes no active role.

The furnace in which the box is heated also involves the use of a substantial amount of energy which is not used directly in the process. In fact, the only items requiring heating to the required temperature are the parts being diffusion coated and the powder in the immediate vicinity of the parts. It is necessary however, that the gas so generated be kept contained around the part for sufficient time to allow this absorption and that the temperature of the part be maintained at that most suitable to allow the production of the required coating.

To date, the heating methods used have been conventional muffle or bell type furnaces and while advances in furnace technology have resulted in some improvements in economics, the basic problem of having to heat up far more material than is necessary still applies.

In the field of metal heat treatment, the use of high frequency induction heating is well-known. In this, the heat is entirely or almost entirely contained within the component being processed. There are further advantages in that distortion is kept to a minimum and also by adjustment of certain factors the generation of heat may be localized. This latter feature cannot be achieved when using conventional radiation (e.g. muffle) type furnaces.

In our U.K. Patent Specification No. 781,594 there is described the application of high frequency heating as a final step in a process for coating a metal with a coating containing chromium by diffusion, in which the metal is first coated with a liquid or pasty composition containing the chromium or chromium alloy in powder form together with a carrier which is solid at room temperature, but becomes liquid or begins to melt at the operating temperature, and which is a halide other than chromium halide. The carrier, for example cryolite, remains bonded to the diffusion coating and has to be removed after the process is complete. Also, because the liquid or pasty composition becomes fused as a whole at the temperature of operation and after use sets as a glass-like mass, it cannot be re-used.

Apart from the above-mentioned disadvantages the process described in the specification had indeed very limited application because it may only be used for small single item components, such as spark plugs, and is not suitable for use on large components.

This process is therefore very extravagant because of the waste of expensive materials. In fact this process has not been used in practice.

It is an object of the present invention to provide a process for the production of diffusion coatings utilizing high frequency induction heating which does not have the disadvantages of the prior art and is of general applicability.

A problem which arises in the application of high frequency induction heating is that of locating the composition which will form the diffusion coating in contact with the part to be chromised. This is solved according to above-mentioned U.K. Patent No. 781,594 by making this composition pasty or liquid, by having a bonding agent, such as ethyl silicate, present and by having a halide carrier which becomes liquid or melts at the temperature of operation thus ensuring close contact with the part being chromised.

The present invention solves the problem in another way, that is by using a loose powder which is kept in contact with the part to be diffusion coated during the diffusion coating.

This loose powder does not form a melt at the operating temperature and, after cooling, may be regenerated by the addition of further active components, such as chromium and halogen-containing materials, so that these are brought back to the original level.

The loose powder is kept in contact with the part being diffusion coated by mechanical means, as more fully described below.

The present invention provides a process for the production of a diffusion coating which comprises contacting a part which is to be diffusion coated with a coating-producing composition while heating by high frequency induction heating, the coating being produced by the heating and the coating-producing composition being a loose powder composition which is retained in contact with the part which is to be diffusion coated by mechanical means during the heating.

The way in which the loose powder is kept in contact with the part being diffusion coated will depend upon the shape of the part being treated,

and indeed whether a localised or over-all treatment is involved.

The high frequency induction heating is preferably provided according to the present invention by a water-cooled induction coil made, for example, from copper. The coil should be as close as reasonably possible to the component being heated. However, a non-metallic separator may be provided between the induction coil and the work-piece without interference with the thermal efficiency; such separator may take the form of heat-resistant tubes of, for example, glass or refractory materials, such as quartz.

The use of such a water-cooled induction coil with or without such a separator enables one to diffusion coat, using a loose powder, a workpiece which may pass through such coil, or around which such coil may be located.

In one embodiment of the present invention, without utilizing such a separator, a part or workpiece of a generally cylindrical nature is diffusion coated on the inside by the steps of: filling it with a diffusion-coating powder, confining the powder within the workpiece in contact with the inner walls by mechanical means; locating the part (tube) inside a high frequency induction heating coil to heat the tube to a temperature sufficient to effect such diffusion coating; optionally moving the said tube with relation to the said coil to effect continuous diffusion coating of the inside of the said tube; and, after cooling, recovering the said diffusion coating powder for regeneration.

In an embodiment utilizing a separator, an outer surface of a cylindrical workpiece may be diffusion coated by the steps of: locating a cylindrical workpiece in a cylindrical separator; providing a collar between the said workpiece and the said separator; introducing a diffusion coating powder into the annulus between the separator and the workpiece so that it is retained in position by the collar; heating the cylindrical workpiece in contact with the powder by an induction coil surrounding the said separator and optionally moving the said cylindrical workpiece with relation to the said coil and/or the said separator; and recovering the powder after cooling for regeneration. It will be understood that the coil may be moved with the separator fixed and *vice versa* depending upon the precise requirements.

It is also possible to use a coil which may be inserted in a cylindrical workpiece and is separated by a separator from the inside surface of the workpiece to be diffusion coated and wherein the powder which provides the diffusion coating on being heated is mechanically retained in the annular space between the separator and the surface to be diffusion coated. This embodiment of the present invention is particularly applicable to the localised chromising of the inside flange of mild steel cell cases for sodium-sulphur batteries as described in more detail below.

The present invention may be applied in principle to the application of diffusion coatings not only of chromium or aluminium or both as mentioned above, but also of other metals or non-metals such as those referred to above. The powder used for the production of the diffusion coating will in general be similar to those used in the prior art pack diffusion processes, with the exception, however, that it should be more active because the process will in general be much faster than a pack diffusion process, e.g. a matter of minutes rather than of hours. One method of many of increasing the activity is by including in the powder a proportion or a higher proportion of a halide of the diffusion element, than is conventionally used.

Thus, for chromising a conventional pack chromising composition may be used, but best results are obtained if the composition contains chromium halide as such, e.g. as $CrCl_3$, rather than having components which form it *in situ*.

A preferred chromising composition for use according to the present invention therefore preferably has a composition falling within the following range:

10—60%, preferably 50%, chromium or chromium or ferrochromium metal powder.

0.1—20%, preferably 10%, chromium halide, such as $CrCl_3$.

Balance, refractory oxide, such as kaolin, titania, magnesia or alumina, preferably alumina 300 mesh.

The temperature for the process of diffusion coating will in general be that conventionally used, but may vary outside the usual range. Thus for chromising the usual range is 700 to 1100°C, but according to the present invention higher temperatures may be used, e.g. up to 1300°C.

The present invention will now be described with reference to certain specific embodiments thereof.

The first embodiment relates to the processing of the interior of metal tubes in long lengths. A tube (11) 2″ (5.08 cm) in diameter and 8′ (243.8 cms) in length, made according to specification C.D.S.I., was taken and a powder (12) containing 50% chromium metal powder, 150 mesh, 10% chromic chloride and a balance calcined alumina 300 mesh was taken and poured into a tube, the object being to provide it with a chromium rich layer of about 40% chromium at the surface and some 100 micron (1×10^{-4} m) in depth. Loose fitting retaining caps (13) were fitted on each end to assist in transport of the tube without loss of powder.

The tube was then fed through an induction coil (14) of suitable shape fitted with a refractory liner (15), e.g. a quartz tube, into the annular space of which was passed a gas containing 95% argon and 5% hydrogen, thus preventing oxidation of the outer surface of the tube. With the inductor energized, the tube was fed through at a rate of 1 inch (2.54 cm) per minutes, a screw rotation being imparted by a suitably disposed roller (16). This screw rotation provides for a more even heating and reduces the possibility of distortion. The temperature attained by the metal

tube was not less than 1100°C. After cooling, the powder was easily tipped out by up-ending the tube and on examination the inside of the tube had a diffusion coating of the desired characteristic. The same experiment was repeated using a powder containing 10% aluminium metal powder 200 mesh, 90% calcined alumina 300 mesh and 0.5% ammonium hydrogen fluoride (NH_4HF_2) and also a somewhat lower temperature. On examination of the inside surface of the tube, there was found to be a diffusion coating of aluminium 75—100 microns ($7.5—10\times10^{-5}$ m) thick.

The procedure of this embodiment is illustrated in Fig. 1 of the accompanying drawings.

This embodiment may be applied to tube of any length, the only limitation being that involved with increasing size and the considerable advantage of the technique is that it avoids the expense and capital outlay of a conventional long muffle furnace and the practical difficulties of handling long narrow processing boxes. The principle may be adapted to a semi-continuous basis.

The second embodiment relates to the processing of the outside of tube, bar and section in long lengths.

The problem in this case is the containment of the powder and active gases around the tube while at temperature.

The way this problem was in principle solved is illustrated in Fig. 2 of the accompanying drawings. A free-flowing powder (21) is fed smoothly under the influence of gravity and vibrator units attached to the feed hopper around the tube (22) as it passed with rotation through an inductor (23), the powder being partially retained by an annular collar (24) and a separator (25), e.g. a quartz tube, so that powder is always in contact with the surface of the workpiece during chromisation. There is an annular space between the collar and the workpiece through which used powder can fall. In the process of heating, some hardening of the powder occurs, which may become attached to the tube assisting in its withdrawal. The essential aspect of the present invention, that a loose powder is retained in contact with the tube during chromising by mechanical means, is, however, fulfilled.

The third embodiment (illustrated in Fig. 3) relates to the case where the induction heating coil is located in the cylindrical workpiece.

This embodiment is described with reference to the application of this technique to local treatment in the case of providing a chromium enriched surface on a seal face that exists within a sodium/sulphur battery cell case. It was found that, at the normal operating temperature of the cell, that is about 350°C, a seal that exists between mild steel and an aluminium gasket is subjected to corrosion. Also there is a tendency for the seal to break down because of the formation of an intermetallic compound between aluminium and iron, namely iron aluminide. The durability of this seal is increased by chromising the part of the cell case involved in this sealing and adjacent to the aluminium gasket. It will also be appreciated that overall chromising of the cell is impractical, if this leads to distortion as we have found that it does, because of the requirements on dimensional tolerances on both the cell case and the associated components that reside within.

The apparatus used is illustrated in Fig. 3 of the accompanying drawings and consists of an outer quartz glass tube (31) with suitable seals at each end (32), e.g. a kapok seal at the lower end and a rubber bung at the upper, and an inner quartz tube (33) down through which passes the inductor coil (34). The cell case (35) being processed is in the annular space so formed and surrounded by a powder (36) where the diffusion coating of chromium is required (37). A wire mesh support (38) is also provided. Through the seals are provided means for the introduction of gas containing hydrogen to prevent oxidation of the steel case during process.

The fourth embodiment illustrated in Fig. 4 shows the application of the present invention to the local diffusion coating of parts, such as tools.

One of the main reasons why metal diffusion techniques have not found a wide and indeed expected application in the field of machined components and tools, for example, has been the difficulty of maintaining the dimensional tolerances and in particular the axiality thereof when totally heated to temperatures above 800°C. Basically this is a problem of distortion due to thermal softening at the temperatures employed. A further factor is that tools and other related parts frequently require a hard surface in a localised area such that heating the whole component is wasteful as well as undesirable.

Illustrated in Fig. 4 of the accompanying drawings is a method involving high-frequency heating for the diffusion coating of a drawing punch to provide a hard wear resistant surface. The punch (41), made from a steel containing 2% carbon, 12% chromium, balance iron, was placed inside a tube of refractory (44) closed at the bottom with a plug (46) and the annular space filled with a powder (42) containing chromium, ferro-titanium, alumina and ammonium iodide. A cap (45) was provided at the top of the refractory tube for the introduction of a gas, such as hydrogen or argon or a mixture of both, in order to remove any air in the pores of the powder. The whole assembly was placed in the coil (43) of a high frequency current generator at a power input sufficient to heat the tool and powder mass to a temperature of not less than 1000°C for a period of three minutes. On cooling down and removing the powder, the punch was found to have a surface hardness of about 1800 V.P.N. and a coating thickness of 12—18 micrometres. Furthermore, the punch was free from linear distortion and could be hardened in the normal way. Also, because of the induction method of diffusion coating and the low thermal mass of the

powder, the cooling down process could be sufficiently fast to achieve satisfactory air-hardening of selected base steels.

The fifth embodiment illustrates the application of the present invention to local diffusion coating of parts, such as pliers or similar manipulating tools. It has been found that the chromium carbide layer produced by classical diffusion techniques has good chemical resistance to various molten metals and alloys, e.g. zinc, aluminium and lead. When applied to tools that are used for manipulating soldered wires or connections in the electronics industry, it greatly reduces the difficulties produced by adhesion of the molten solder to the working surfaces of the tool.

Illustrated in Fig. 5 of the accompanying drawings is a method of heating the working faces of a pair of pliers to provide a solder resistant surface. The pliers (55) are typically made from a 0.5—0.6% carbon steel. After insertion into a quartz tube (51), the annular space was filled with a powder (52) containing chromium, alumina and ammonium chloride. After first ensuring that the powder was firmly compressed, the end of each tube was sealed using an alumina cement (53). The pliers were then placed in a double coil (54) of a high frequency generator at a power input sufficient to heat the pliers and powder mass to a temperature of not less than 1000°C for a period of ten minutes. On cooling down and removing the powder the pliers were found to have a chromium carbide diffusion coating 12—15 micrometres thick which had excellent resistance to attack by molten metals and alloys.

This was achieved without distortion and without damage to the insulating plastics coating on the hand grip section. Furthermore, the pivots functioned satisfactorily. These features may only be obtained by the use of the induction heating method described.

The regeneration of the powder used for the chromising according to the above embodiments may be achieved by bringing the contents of the various components of the powder up to the original specification.

Thus, in a typical case, the original ingredients of the powder before use are:—

50% chromium as metal, 150 mesh
10% chromium (III) chloride
Balance alumina, 300 mesh

After the diffusion step, using high frequency heating, the average analysis for chromium recorded for the used powder was found to be 51.2%. Therefore, to 1 kg of the used powder, was added the following:—

100 gm chromium as metal, 150 mesh
20 gm chromium (III) chloride
50 gm alumina, 300 mesh

The powder was then mixed thoroughly and the average analysis for chromium recorded was 52.6%. This powder was then ready for re-use. It is clear that waste of valuable materials is thus obviated.

Claims

1. A process for the production of a diffusion coating which comprises contacting a part which is to be diffusion coated with a coating-producing composition while heating by high frequency induction heating, the coating being produced by the heating and the coating-producing composition being a loose powder composition which is retained in contact with the part which is to be diffusion coated by mechanical means during the heating.

2. A process as claimed in claim 1 wherein the induction heating is provided by means of an induction coil, optionally provided with a separator, the coil being such that a part being diffusion coated may be located co-axially therewith.

3. A process as claimed in claim 1 or claim 2 for diffusion coating an inner surface of a part of a generally cylindrical nature comprising: filling the part with a diffusion coating powder; confining the powder within the part in contact with the inner surface by mechanical means; locating the part inside a high frequency induction heating coil to heat the part to a temperature sufficient to effect such diffusion coating; optionally moving the said part with relation to the said coil to effect continuous diffusion coating of the inside of the said part; and after cooling, recovering the said diffusion coating powder for regeneration.

4. A process as claimed in claim 1 or claim 2, for coating an outer surface of a cylindrical part utilizing an induction coil with a separator comprising: locating a cylindrical part in a cylindrical separator; providing a collar between the said part and the said separator; introducing a diffusion coating powder into the annulus between the separator and the part so that it is retained in position by the collar; heating the cylindrical part in contact with the powder by an induction coil surrounding the said separator and optionally moving the said cylindrical part with relation to the said coil and/or the said separator; and recovering the powder after cooling for regeneration.

5. A process as claimed in claim 1 or claim 2 for coating an inner surface of a part of a generally cylindrical nature utilizing an induction coil with a separator wherein the diffusion coating powder is mechanically retained in an annular space between the separator and the surface to be diffusion coated.

6. A process as claimed in claim 5 wherein the part is a mild steel cell case for a sodium-sulphur battery and the process provides localised diffusion coating for a flange provided in the said case for sealing engagement.

7. A process as claimed in any of claims 1 to 6 wherein the diffusion coating process is a chromising process.

8. A process as claimed in claim 7 wherein the chromising composition in loose powder form contains chromium halide.

9. A process as claimed in claim 1 substantially as herein described with particular reference to any one of the accompanying drawings.

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